

Creep of $(\text{La}_{0.55}\text{Sr}_{0.45})_{0.99}\text{Mn}_{1-y}\text{Ga}_y\text{O}_3^\dagger$

Jules Routbort,^{*a} James Ralph,^a R. E. Cook,^a C. Clauss^b and A. R. de Arellano-López^b

^a Argonne National Laboratory, Argonne IL 60439, USA. E-mail: Routbort@anl.gov;
Fax: +1 630 252 4798; Tel: +1 630 252 5065

^b University of Sevilla, 41080 Sevilla, Spain. E-mail: aral@us.es; Fax: +34 95461 2097;
Tel: +34 95459 2894

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Steady-state compressive creep was measured in $(\text{La}_{0.55}\text{Sr}_{0.45})_{0.99}\text{Mn}_{1-y}\text{Ga}_y\text{O}_3$ at temperatures from 1200 to 1270 °C in air at stresses (σ) from 13 to 40 MPa. The Ga concentration was $y = 0, 0.05, \text{ and } 0.10$. Strains to 0.14 were obtained. In the creep equation for strain rate, $\dot{\epsilon} = A^n \exp(-Q/RT)$, stress exponents (n) were between 1.3 and 1.7, indicating that diffusional flow is the dominant creep mechanism, and the activation energy (Q) was found to vary from 355 kJ mol⁻¹ for $y = 0$ to 485 kJ mol⁻¹ for $y = 0.10$.

I. Introduction

The solid-oxide fuel cell is under development for residential and auxiliary power units, as well as larger industrial power applications. The cathode for solid-oxide fuel cells must exhibit good electrical conductivity, catalytic properties for oxygen dissociation, and acceptable ionic conductivity.¹

$\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM) has very good electrical conductivity and catalytic properties for oxygen dissociation, but its ionic conductivity is low. In addition, LSM is compatible with the yttria-stabilized zirconia electrolyte. Doping with Sr increases the electronic conductivity because of Mn oxidation.^{2,3} Recently, it has been postulated that doping with Ga on the B site alters the internal equilibrium and increases the oxygen vacancy concentration. Vaughey, *et al.* suggested that a concomitant increase in the ionic conductivity was responsible for the observed lower cathodic overpotentials.¹ The increase in ionic conductivity is attributed to the tendency for Ga to have four-fold coordination that allows the Mn cations an alternative to oxidation, *e.g.*, reduction of coordination number.¹ It is the tendency of Ga to have four-fold coordination that lies at the core of the high ionic conductivity of $(\text{La}, \text{Sr})(\text{Mg}, \text{Ga})\text{O}_3$.^{4,5}

The mechanical properties of LSM are not well known, but are important for the long-term operation of fuel cells. Steady-state creep could be responsible for degradation of contacts between cells. The effect of Ga additions to LSM on the creep process is important.

If the mechanism of steady-state creep is known to be the result of a diffusion-controlled process, measurements can be used to extract information on the minority defects that also control other important kinetic processes, such as sintering and grain growth. The connection between steady-state creep and the diffusion of the rate-controlling species can be obtained from a generalized creep equation for steady-state strain rate $\dot{\epsilon}$:

$$\dot{\epsilon} = A \left(\frac{b}{d}\right)^h \frac{\mu b}{RT} \left(\frac{\sigma}{\mu}\right)^n D^{\text{eff}}, \quad (1)$$

where A is a model-dependent constant, b is the Burger's vector, d is the grain size, μ is the shear modulus, σ is the stress, D^{eff} is the

effective diffusion constant, and RT has its usual meaning. The parameter h depends on the diffusion path, *e.g.*, $h = 2$ for volume diffusion or 3 for grain-boundary diffusion. The effective diffusion coefficient can be complex; it depends on both cation and anion diffusion and whether the overall composition or the composition along each path is constant.⁶ In general, if the diffusion coefficient of one species is much lower than that of the other species, the effective diffusion coefficient will be equal to the lowest. If, in addition, one diffusion path dominates (either volume or grain boundary), D^{eff} in eqn. (1) can be greatly simplified.

Successful creep and diffusion studies of minority defects in transition-metal binary oxides were conducted and documented in the period of approximately 1970–90 (see, for example, ref. 7). However, such studies in more complex oxides, such as high-temperature superconductors and other perovskite-structured oxides that have electronic applications, have only met with limited success. Reasons such as lack of reliable creep and diffusion data and the complex nature of the defects and their diffusion paths can be cited. Nevertheless, there have been some notable successes. A recent creep investigation of LSM in which $[\text{Sr}] = 0.1, 0.2, \text{ and } 0.3$ and oxygen partial pressure (P_{O_2}), was varied, successfully described the results on the basis of a defect-chemistry model. The model indicated that cation vacancies controlled the creep when there was no A-deficiency, and that oxygen vacancies were rate controlling for A-site deficient LSM at high P_{O_2} for $[\text{Sr}] = 0.1$ and 0.2. The creep activation energy was 530 ± 40 kJ mol⁻¹ for $[\text{Sr}] = 0.2$ in air in the temperature range 1165–1265 °C. In addition, examining the shift in the crossover in the Brouwer diagram with composition, the investigators suggested that La vacancy controls creep in the cation region.² Earlier creep measurements on the LSM system measured Q values ≈ 460 –490 kJ mol⁻¹ which were suggested to be the result of cation-vacancy diffusion.^{8,9}

The creep of Ga-doped LSM has not been investigated. However, two creep studies of the Mg-doped $(\text{La}, \text{Sr})\text{GaO}_3$ (LSGM) system have been published. One was for $[\text{Sr}] = 0.2$ and $[\text{Mg}] = 0.15$, and the other was for $[\text{Sr}] = 0.1$ and $[\text{Mg}] = 0.2$;^{10,11} the activation energies were 521 and 426 kJ mol⁻¹, respectively. Oxygen tracer diffusion has been measured in LSM and found to have an activation energy in the range of 253–350 kJ mol⁻¹ in the temperature range of 700–1100 °C.^{12,13} These activation energies are considerably

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lower than the Q values measured for creep. Cook *et al.*² rationalized the discrepancy between the activation energies determined from creep (in the anion-vacancy-controlled creep region) and anion self diffusion by attributing it to the fact that the former measured volume diffusion whereas the latter might have measured grain-boundary diffusion. Recently, Schulz and Martin have reported tracer diffusion data for Y, Fe, and Cr in $(\text{La}_{0.8}\text{Sr}_{0.2})(\text{Ga}_{0.8}\text{Mg}_{0.2})\text{O}_{2.8}$.^{14,15} The reported activation energies for cation impurity diffusion were between 180 and 250 kJ mol^{-1} . Subsequently, Martin¹⁶ presented results that showed that all three of the cation impurities fall on the same Arrhenius plot. The value of Q for cation tracer diffusion, albeit for impurity diffusion, is much lower than the activation energies measured in creep. This obviously presents a problem for the interpretation of creep studies.

These systems have many compositional variables: La/Sr ratio, B site occupied by Mg or Mn, Ga concentration, and cation and anion nonstoichiometry. Experimental variables include microstructure, particularly grain size because it affects creep, P_{O_2} , and temperature. Investigating all of these variables would be a prodigious task. Hence, we have narrowly focused the goals of this investigation to determine if Q for creep is dependent on [Ga] and/or [Sr]. We have chosen the intermediate composition $(\text{La}_{0.55}\text{Sr}_{0.45})_{0.99}\text{Mn}_{1-y}\text{Ga}_y\text{O}_3$ so our results would fill in gaps at higher concentrations of Sr. Mn was chosen as the B site cation because most creep studies have been performed on this system, and it is of technological interest as a cathode for a solid-oxide fuel cell.

II. Experimental details

a. Sample preparation

Powders produced by glycine nitrate combustion synthesis were calcined in air at 1250 °C for 1 h. X-ray diffraction indicated that the powders were phase pure. The calcined powders were ground and ball-milled in ethanol for 1 week. The final particle size was between 1 and 2 μm . Powders were sieved and pressed into bars under a 4100 kg load. The bars were sintered at 1500 °C in air for 6 h. Samples were $\geq 98\%$ of theoretical density, final grain sizes were $\approx 5\text{--}10 \mu\text{m}$. Scanning electron photomicrographs of the three microstructures representing the three compositions are shown in Fig. 1. The grain sizes remained constant during creep testing.

b. Creep testing

Compressive creep experiments were performed under a constant load in air with a previously described apparatus.¹⁷ Both the load and the temperature could be changed. Axial sample dimension changes were measured with an extensometer. The decrease in sample length is converted into a strain (ϵ) whose derivative with time is used to calculate $\dot{\epsilon}$. Samples $6.3 \times 2.7 \times 2.7 \text{ mm}$ were deformed into steady state (defined as when the slope of $\dot{\epsilon}$ vs. ϵ becomes constant). Furthermore, steady state was independent of intermediate changes in temperature or load. That is, after a change in load or temperature that would lead to the establishment of a new steady state, followed by a return to the original load or temperature, the load and/or temperature returned to its original value, *i.e.*, the slope will be the same as the original one. Applied stresses were between 13 and 40 MPa, and strains were restricted to < 0.15 . The values of stress quoted are the load divided by the initial area. The correction to account for a changing area is $< 15\%$.

III. Results

A typical creep curve measured for an undoped LSM sample, $(\text{La}_{0.55}\text{Sr}_{0.45})_{0.99}\text{MnO}_3$, is shown in Fig. 2. The results are

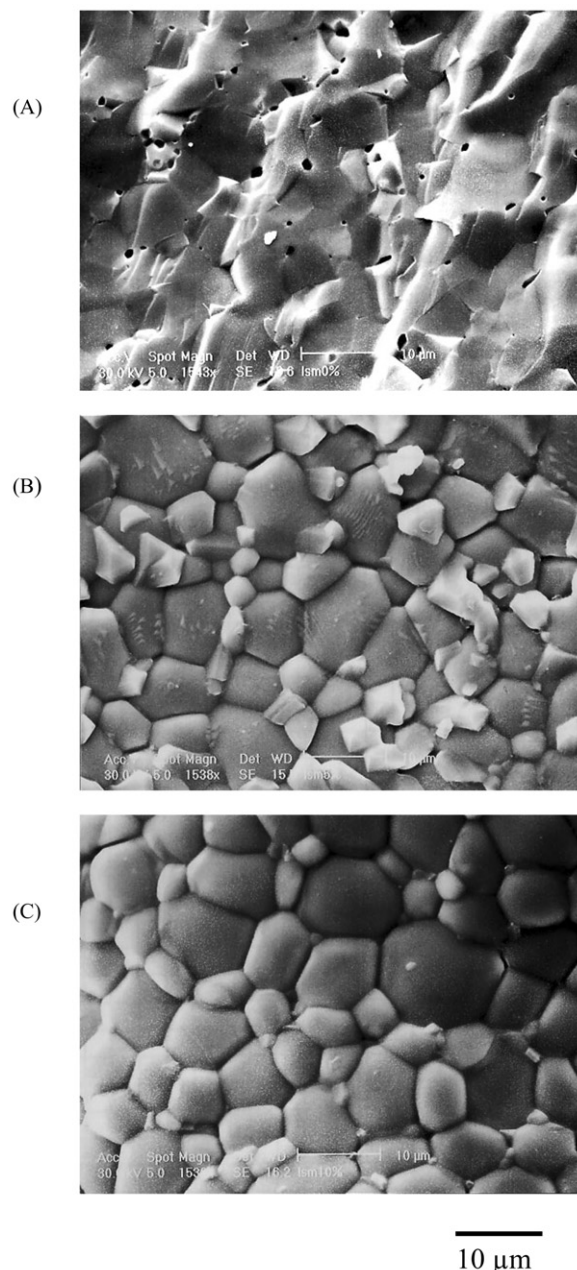


Fig. 1 Scanning electron photomicrographs of (A) fractured surface of LSM, (B) thermally etched surface of LSM for $y = 0.05$, and (C) thermally etched surface of LSM for $y = 0.10$.

plotted as $\dot{\epsilon}$ vs. ϵ . In this experiment, the temperature was changed five times at a constant stress to measure five values of Q , which ranged between 333 and 355 kJ mol^{-1} , and the stress was changed from 26 MPa to 20 MPa at 1250 °C to measure $n \approx 1.5$. As can be seen from the figure, the slopes of the $\dot{\epsilon}$ vs. ϵ curves are unchanged when the initial temperature is used. This is clear evidence of the establishment of a steady state that implies that the structure remains constant, in agreement with the observation that grain size does not change. A transient precedes each steady-state strain rate. Creep data for the 5%-Ga-doped sample, $(\text{La}_{0.55}\text{Sr}_{0.45})_{0.99}\text{Mn}_{0.95}\text{Ga}_{0.05}\text{O}_3$, are shown in Fig. 3. Again, the slopes of the $\dot{\epsilon}$ vs. ϵ curves are constant indicating that steady-state creep has been achieved. Activation energies obtained from five temperature changes at 20 MPa were between 392 and 424 kJ mol^{-1} , and changing stress from 20 to 40 MPa led to $n \approx 1.7$.

Because steady-state conditions were achieved, the values of $\dot{\epsilon}$ can be extrapolated to $\epsilon = 0$. Arrhenius plots can be constructed from temperature jumps at constant stress. Such plots

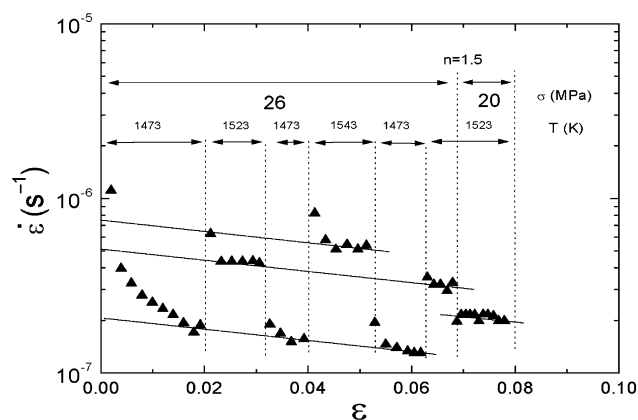


Fig. 2 Creep data plotted as $\dot{\epsilon}$ vs. ϵ for undoped LSM, $(\text{La}_{0.55}\text{Sr}_{0.45})_{0.99}\text{MnO}_3$. Values of σ , T , and n , are shown.

are shown in Fig. 4. The resultant activation energies are plotted in Fig. 5 and presented in Table 1. The plots for each composition were made at stresses that varied from 13 to 26 MPa. Although there is only a factor of two difference in stress, the possibility that the creep mechanism is a function of stress cannot be ruled out until experiments over a wider range of stresses can be performed.

Finally, the measured Q values for $(\text{La}_{0.55}\text{Sr}_{0.45})_{0.99}\text{MnO}_3$ can be compared with values for all of the compositions of undoped LSM from the literature cited in Table 1. This investigation has contributed the Q at $[\text{Sr}] = 0.45$; the plot is shown in Fig. 6. It is worth mentioning that the value of Q measured for the creep of $[\text{Sr}] = 0.20$ reflects anion-controlled diffusion and cannot be compared with other results which, according to the defect model,² represent cation diffusion. This is probably best illustrated with a schematic Brouwer diagram for LSM as shown in Fig. 7. The crossover point between anion vacancy and cation vacancy control shifts to higher P_{O_2} as $[V''_{\text{La}}]$ decreases.²

IV. Discussion

The stress exponents measured in this investigation ranged between 1.3 and 1.7 and were somewhat higher than values reported for the other LSM materials listed in Table 1. However, the values reported here were obtained from only one stress jump per composition because the emphasis of this investigation was the determination of the activation energy.

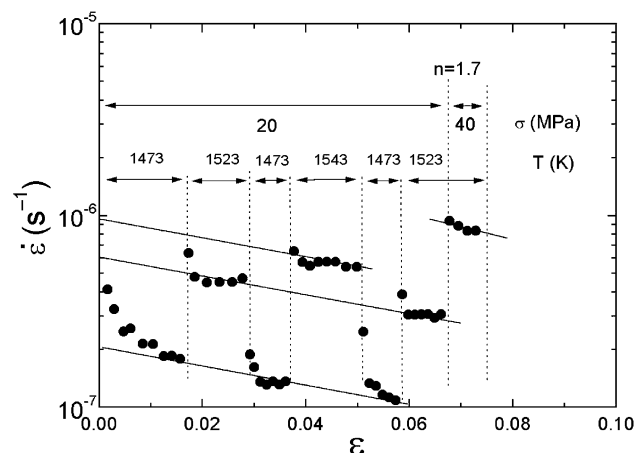


Fig. 3 Creep data plotted as $\dot{\epsilon}$ vs. ϵ for $(\text{La}_{0.55}\text{Sr}_{0.45})_{0.99}\text{Mn}_{0.95}\text{Ga}_{0.05}\text{O}_3$. The values of σ , T , and n are shown.

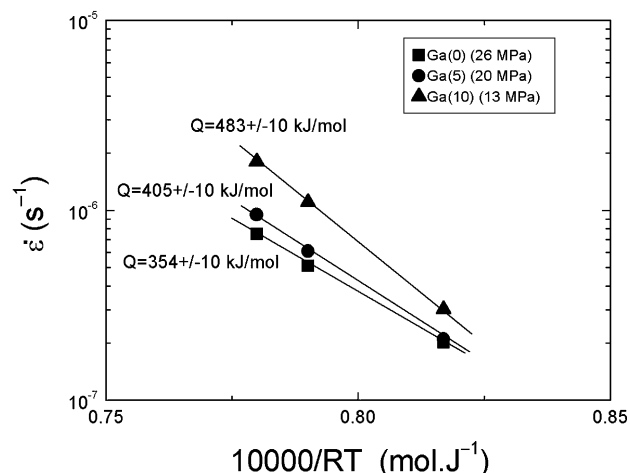


Fig. 4 Arrhenius plots for undoped LSM and 5 and 10% Ga-doped LSM. Values of stresses for which plots were made are shown in the legend. Uncertainties shown are calculated from the least-square fits to the Arrhenius plots; they do not include uncertainties in temperatures and strain rates.

Therefore, the scatter in the n values could be large. Nevertheless, values of n between 1 and 2 are indicative of diffusional flow.¹⁸ Therefore, the rate-controlling step will be the diffusion of the slowest-moving species. It should be noted that the previous creep studies identified the deformation mechanism as grain-boundary sliding, in which the strain is accommodated by volume diffusion. Self diffusion for these systems has not been extensively measured although anion self diffusion in LSM has been measured for $[\text{Sr}] = 0.05\text{--}0.50$.^{12,13} Final judgment must await cation and anion self-diffusion measurements and creep measurements over a range of P_{O_2} on the same compositions, carefully controlling both cation and anion nonstoichiometry.

Creep studies have a practical aspect, namely dimensional stability of the electrode. If an extrapolation of these results were made to approximate operating conditions of a solid-oxide fuel cell (e.g., 800 °C and 2 MPa), it would take ≈ 32 years to accumulate 0.1% strain. An extrapolation of over 400 °C and a factor of 10 in stress is to be viewed cautiously.

Attention now focuses on the variation of the activation energy for creep with $[\text{Sr}]$, as shown in Fig. 6. Recall that the datum for $[\text{Sr}] = 0.2$ was obtained on an A-site deficient LSM in which anion vacancy diffusion controls creep. It cannot be considered with the open circles measured for LSM in which cation diffusion controls creep. The data represented

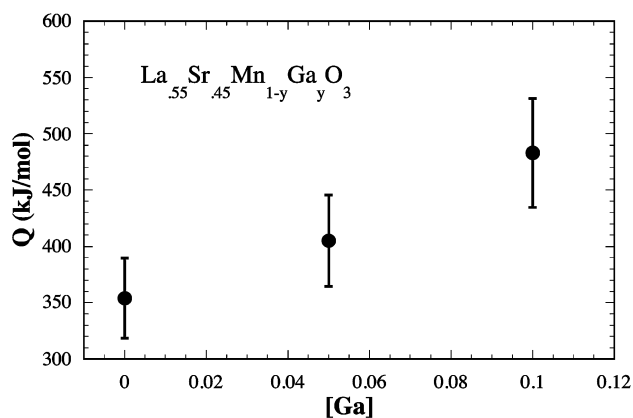


Fig. 5 Variation of activation energy for creep as a function of $[\text{Ga}]$. Error bars reflect estimated uncertainties in strain rate, and temperature.

Table 1 Tabulated creep data for undoped and Ga-doped LSM, and LSGM

Material	$T/^\circ\text{C}$	n	$Q/\text{kJ mol}^{-1}$	Ref.
$(\text{La}_{0.8}\text{Sr}_{0.2})(\text{Ga}_{0.85}\text{Mg}_{0.15})\text{O}_3$	1200–1300	≈ 1	521 ± 23	10
$\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$	1150–1300	1.1	490 ± 30	8
$\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$	1150–1300	1.1	475 ± 25	9
$\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$	1150–1300	0.9	460 ± 15	9
$\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$	1150–1300	1.3	530 ± 40	2
$(\text{La}_{0.9}\text{Sr}_{0.1})(\text{Ga}_{0.8}\text{Mg}_{0.2})\text{O}_3$	950–1350	1.5	426 ± 9	11
$(\text{La}_{0.55}\text{Sr}_{0.45})_{0.99}\text{MnO}_3$	1200–1270	≈ 1.5	355 ± 10	This study
$(\text{La}_{0.55}\text{Sr}_{0.45})_{0.99}\text{Mn}_{0.95}\text{Ga}_{0.05}\text{O}_3$	1200–1270	≈ 1.7	405 ± 10	This study
$(\text{La}_{0.55}\text{Sr}_{0.45})_{0.99}\text{Mn}_{0.9}\text{Ga}_{0.1}\text{O}_3$	1200–1270	≈ 1.3	485 ± 10	This study

by the open circles is fitted with the model for cation-vacancy-controlled creep in the following manner. Eqn. (1) can be rewritten as

$$\dot{\epsilon} = BD_0 \exp(-Q/RT) = B' [V_{\text{La}}'''] \exp(-Q/RT) \quad (2)$$

where $[V_{\text{La}}''']$ is the concentration of the rate-controlling defect. This leads immediately to the following expression for Q as a function of $[V_{\text{La}}''']$ with B'' and A' as constants:

$$Q = B'' \ln[V_{\text{La}}'''] + A'. \quad (3)$$

The cation vacancy relation from ref. 2 at $P_{\text{O}_2} = 2.13 \times 10^4$ Pa (air) is

$$[V_{\text{La}}'''] = \frac{0.4 + 0.03[\text{Sr}'_{\text{La}}] - [\text{Sr}'_{\text{La}}]^2}{6[\text{Sr}'_{\text{La}}]} \quad (4)$$

Eqn. (4) was then fitted to the weighted data shown in Fig. 6. A very simple physical interpretation for the decrease in Q as $[\text{Sr}]$ increases might be based on the fact that Sr is larger than La and would, therefore, expand the lattice when substituted for La in LSM. If creep is controlled by the diffusion of cation vacancies and the lattice is expanded, Q would decrease as a result of less binding between the ring atoms that surround the jumping cation. The actual details would depend on exactly which cation vacancies are involved, cation nonstoichiometry, and the path of the atomic jump. For example, would an A-site vacancy diffuse by moving to a B site? This idea would imply that there should be a gradual decrease in Q with increasing $[\text{Sr}]$. Clearly, creep experiments for various Sr concentrations should be performed.

Fig. 5 indicates that the activation energy for creep increases with increasing $[\text{Ga}]$. As mentioned in the introduction, doping

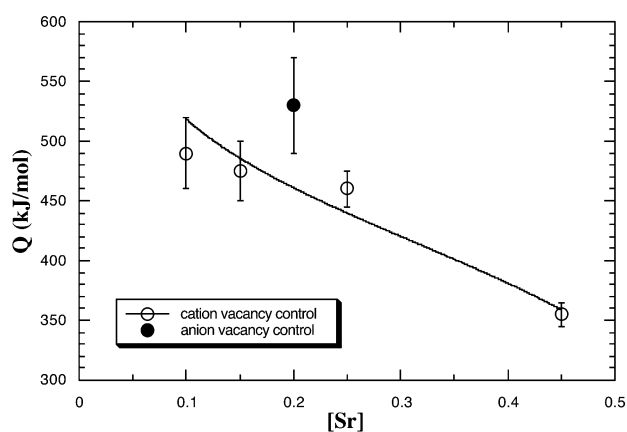


Fig. 6 Variation of activation energy for creep as a function of $[\text{Sr}]$ for undoped LSM. The filled point represent creep in the anion-vacancy-controlled region, whereas the open points represent cation-diffusion-controlled creep.² References for data for $[\text{Sr}] < 0.45$ are given in Table 1. The solid line is the weighted fit of the cation model² to the open points.

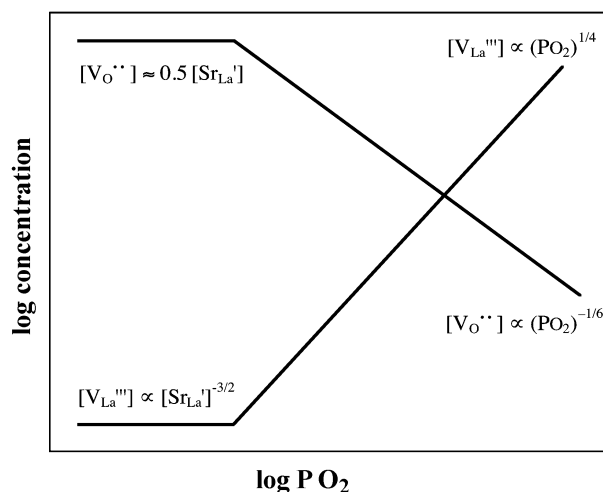


Fig. 7 Schematic Brouter diagram for cation and anion vacancies in LSM system (after ref. 2).

with Ga, which has a preference for a coordination number lower than six, allows LSM to alter the internal equilibrium, offering an alternative to Mn oxidation, namely, reduced coordination.¹ A significant number of oxygen vacancies can then be formed to compensate charge.^{19,20} When the oxygen-ion vacancy concentration becomes large, the vacancies might cluster, and attract cation vacancies. The additional attractive force would increase the self-diffusion activation energy and increase the Q for creep.

This investigation has not resolved the apparent discrepancy between the high activation energies measured for creep and the lower activation energies measured for impurity diffusion in the $(\text{La},\text{Sr})(\text{Mg},\text{Ga})\text{O}$ system. It might be that the diffusion path for the impurity cation is different from the native cation, resulting in different activation energies for impurity and self diffusion. However, it should be noted that diffusion and creep measurements were not performed on the same material. Impurity diffusion^{14,15} was performed for $(\text{La}_{0.8}\text{Sr}_{0.2})(\text{Ga}_{0.8}\text{Mg}_{0.2})\text{O}_{2.8}$, whereas the creep was measured in $(\text{La}_{0.8}\text{Sr}_{0.2})(\text{Ga}_{0.85}\text{Mg}_{0.15})\text{O}_3$.¹⁰ Therefore, not only was the Ga/Mg ratio different in the two cases, but so was the oxygen stoichiometry. The A- and/or B-site deficiencies could well have been different. This work has shown that the activation energy for creep depends on $[\text{Ga}]$ and on $[\text{Sr}]$ in the undoped system that contains Mn in the cation-vacancy diffusion-controlled regime.

It is clear that additional creep, and cation and anion self-diffusion experiments will be required to obtain a complete picture and to relate the results to defect chemistry. The work described above should be viewed as an initial investigation. A complete investigation would involve careful A- and B-site doping, varying cation and anion nonstoichiometry, and measurements over a wider temperature range and, for creep, over a wider stress region.

V. Conclusions

Although much work remains to be done, this investigation clearly shows that the activation energy for creep depends on the concentration of Ga. All of the previous creep studies indicate that creep is controlled by grain-boundary sliding and the strain is accommodated by diffusion. Therefore, we would predict that the activation energy for self diffusion of the rate-controlling cation would also be a function of $[\text{Ga}]$. The functional dependence of Q on $[\text{Sr}]$ in the undoped system is consistent with cation-vacancy-controlled creep.²

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